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# **Prepn. of chitosan salt of absorptive properties e.g. for diapers - comprises recovery of chitosan salt from mixt. of mono- and multi-basic acid(s), water and water-insoluble chitosan and opt. heat treating**

**Patent Number : GB2296250**

*International patents classification : A61L-000/00 A61L-015/60 C08B-000/00 C08B-037/08 A61F-000/00 B01J-000/00 A61L-015/28 A61L-015/42*

**• Abstract :**

GB2296250 A Prepn. of a water-swellaable, water-insoluble chitosan salt (I), having an initial Absorbency under Load (AUL) value 14 g/g, comprises: (i) formation of a mixt. of pH 2-6.5, of (a) water-insoluble chitosan, (b) water and (c) an acid from mono- and multibasic acids of pKa, below 6, all pKa being more than 5.5 and n being an integer more than 1; and (ii) recovery of (I). Opt. (1) after recovery of the water-soluble chitosan salt, treatment under humid conditions or at a temp. and for a period follows to obtain (I); or (2) the recovered chitosan salt comprises an amt. of the original crystalline structure to give (I). Also claimed is (I) described.

USE - (I) is suitable for personal care prods., e.g. diapers, training pants, adult incontinence prods. and feminine care prods..

ADVANTAGE - Natural based (I) has absorptive properties similar to synthetic, highly absorptive materials. (Dwg. 1/1)

GB2296250 B A water-swellaable, water-insoluble chitosan salt wherein the chitosan salt exhibits an initial Absorbency Under Load value of at least about 14 grams per gram. (Dwg. 1)

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<b>(21) International Application Number:</b> PCT/US95/16191 <b>(22) International Filing Date:</b> 14 December 1995 (14.12.95) <b>(30) Priority Data:</b> 08/362,395 22 December 1994 (22.12.94) US <b>(71) Applicant:</b> KIMBERLY-CLARK CORPORATION [US/US]; 401 North Lake Street, Neenah, WI 54956 (US). <b>(72) Inventors:</b> DUTKIEWICZ, Jacek; 2220 West Seneca Drive, Appleton, WI 54914 (US). NING, Xin; 12431 Crabapple Meadow Way, Alpharetta, GA 30201 (US). QIN, Jian; 1602 East Cranberry Drive, Appleton, WI 54915 (US). SUN, Tong; Apartment 8, 1747 Golf Bridge Drive, Neenah, WI 54956 (US). <b>(74) Agents:</b> SCHENIAN, John, R. et al.; Kimberly-Clark Corpora- tion, 401 North Lake Street, Neenah, WI 54956 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> CHITOSAN SALTS AND PROCESS FOR THE PREPARATION THEREOF		
<b>(57) Abstract</b> <p>Disclosed is a method for producing a water-swellaable, water-insoluble chitosan salt having improved absorption properties. The method involves forming a mixture of a chitosan, water, an acid, and, optionally, a crosslinking agent, recovering the formed chitosan salt from the mixture and, optionally, treating said recovered chitosan salt with heat or under humid conditions.</p> <div data-bbox="1136 1092 1461 1848"></div>		

## CHITOSAN SALTS AND PROCESS FOR THE PREPARATION THEREOF

5 The present invention relates to chitosan salts having improved absorbent properties.

10 The use of water-swellaable, generally water-insoluble absorbent materials, commonly known as superabsorbents, in disposable absorbent personal care products is known. Such absorbent materials are generally employed in absorbent products such as  
15 diapers, training pants, adult incontinence products, and feminine care products in order to increase the absorbent capacity of such products while reducing their overall bulk. Such absorbent materials are generally present in absorbent products in a fibrous matrix, such as a matrix of wood pulp  
20 fluff. A matrix of wood pulp fluff generally has an absorbent capacity of about 6 grams of liquid per gram of fluff. The absorbent materials described above generally have an absorbent capacity of at least about 10, preferably of about 20, and often  
25 of up to 100 times their weight in water. Clearly, incorporation of such absorbent materials in personal care products can reduce the overall bulk while increasing the absorbent capacity of such products.

25 A wide variety of materials has been described for use as absorbent materials in such personal care products. Such materials include natural-based materials such as agar, pectin, gums, carboxyalkyl starch, and carboxyalkyl cellulose, as well as synthetic materials such as polyacrylates, polyacrylamides,  
30 and hydrolyzed polyacrylonitrile. While the natural-based absorbent materials are known for use in personal care products, they have not gained wide usage in such products. The natural-based absorbent materials have not gained wide usage in personal care products, at least in part, because their  
35 absorbent properties are generally inferior compared to the synthetic absorbent materials, such as the polyacrylates. Specifically, many of the natural-based materials tend to form soft, gelatinous masses when swollen with a liquid. When

Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description and the drawing. The claims are intended to be understood as a first, non-limiting approach to defining the invention in general terms.

The present invention relates to chitosan salts having improved absorbent properties. Specifically, the present invention relates to chitosan salts having an improved ability to absorb liquid while under an external pressure and a process for the preparation thereof.

Disclosed is a method for producing a water-swellaable, water-insoluble chitosan salt having improved absorption properties. The method involves forming a mixture of a chitosan, water, an acid, and, optionally, a crosslinking agent, recovering the formed chitosan salt from the mixture and, optionally, treating said recovered chitosan salt with heat or under humid conditions.

In one aspect, the present invention concerns a water-swellaable, water-insoluble chitosan salt. The chitosan salt is characterized in that it exhibits an effective initial Absorbency Under Load (AUL) value.

One embodiment of the present invention concerns a water-swellaable, water-insoluble chitosan salt that exhibits an initial Absorbency Under Load value of at least about 14 grams per gram.

In another aspect, the present invention further concerns a process for preparing a water-swellaable, water-insoluble chitosan salt that exhibits an effective initial Absorbency Under Load value.

One process of the present invention comprises the steps of preparing a mixture comprising a water-insoluble chitosan, water, and an acid. A chitosan salt is formed and is recovered

5 treated under humid conditions and for a time effective to render the chitosan salt water swellable and water insoluble, wherein the water-swellable, water-insoluble chitosan salt preferably exhibits an initial Absorbency Under Load value of at least about 14 grams per gram.

10 Another embodiment of such a process comprises forming a mixture comprising a water-insoluble chitosan salt, water, an acid selected from the group consisting of monobasic acids having a  $pK_{a1}$  less than about 6 and multibasic acids having a  $pK_{a1}$  less than about 6 and all  $pK_{an}$  greater than about 5.5, wherein n is an integer greater than 1, and a crosslinking agent. The mixture may have an equilibrium pH between about 2 and about 6.5. A chitosan salt is formed and recovered, along with the  
15 crosslinking agent, from the mixture. The recovered chitosan salt is water swellable and water insoluble and preferably exhibits an initial Absorbency Under Load value of at least about 14 grams per gram.

20 Another process of the present invention comprises preparing a chitosan salt from a chitosan in a mixture comprising a nonsolvent and recovering the chitosan salt from the mixture, wherein the chitosan salt comprises an amount of the original crystalline structure of the chitosan to be effective so that  
25 the chitosan salt exhibits an effective initial Absorbency Under Load.

30 One embodiment of such a process comprises preparing a mixture comprising a chitosan comprising an original crystalline structure, water, an acid selected from the group consisting of monobasic acids having a  $pK_{a1}$  less than about 6 and multibasic acids having a  $pK_{a1}$  less than about 6 and all  $pK_{an}$  greater than about 5.5, wherein n is an integer greater than 1, and a nonsolvent that is miscible with water and in which both  
35 chitosan and the chitosan salt to be formed are insoluble. The water and the nonsolvent are preferably used in amounts in the mixture effective to result in the chitosan and the chitosan salt to be formed not being soluble in the mixture. The mixture

When many of the acetyl groups of chitin are removed by treatment with strong alkalis, the product is chitosan, a high molecular weight linear polymer of 2-deoxy-2-amino glucose. The properties of chitosan relate to its polyelectrolyte and polymeric carbohydrate character. Thus, it is generally insoluble in water, in alkaline solutions at pH levels above about 6.5, or in organic solvents. It generally dissolves readily in dilute solutions of organic acids such as formic, acetic, tartaric, and citric acids, and also in dilute mineral acids, except, for example, sulfuric acid. In general, the amount of acid required to dissolve chitosan is approximately stoichiometric with the amino groups.

Chitosan is thus not a single, definite chemical entity but varies in composition depending on the conditions of manufacture. It may be equally defined as chitin sufficiently deacetylated to form soluble amine salts. Solutions of chitosan are generally highly viscous, resembling those of natural gums. The cationic properties of the polymer lead to the formation of complexes with anionic polyelectrolytes.

The chitosan used herein is suitably in relatively pure form. Methods for the manufacture of pure chitosan are well known. Generally, chitin is milled into a powder and demineralized with an organic acid such as acetic acid. Proteins and lipids are then removed by treatment with a base, such as sodium hydroxide, followed by chitin deacetylation by treatment with concentrated base, such as 40 percent sodium hydroxide. The chitosan formed is washed with water until a generally neutral pH is reached.

Suitable chitosans are commercially available from numerous vendors. Exemplary of a commercially available chitosan is a partially deacetylated chitin, having a degree of acetylation of about 0.2 and a viscosity as a 1 weight percent aqueous solution of about 3600 mPa·s (3,600 centipoise), available from the Vanson Company.



of chitosan and an acid, such as an organic acid or an inorganic acid. Examples of chitosan salts formed with an inorganic acid include chitosan hydrochloride, chitosan hydrobromide, chitosan phosphate, and mixtures thereof. Examples of chitosan salts  
5 formed with an organic acid include chitosan formate, chitosan acetate, chitosan propionate, chitosan chloroacetate, chitosan hydroxyacetate, chitosan butyrate, chitosan isobutyrate, chitosan acrylate, and mixtures thereof. It is also suitable to form a chitosan salt using a mixture of acids including, for  
10 example, both inorganic and organic acids. The most suitable chitosan salts include chitosan hydrochloride, chitosan formate, chitosan acetate, chitosan propionate, and mixtures thereof.

Chitosans useful in preparing the chitosan salts of the present  
15 invention generally have an average degree of acetylation (D.A.) from 0 to about 0.5, suitably from 0 to about 0.4, and more suitably from 0 to about 0.3. The degree of acetylation refers to the average number of acetyl groups present on the anhydroglucose unit of the chitosan material. Generally, the  
20 maximum average number of acetyl groups that may be present on the anhydroglucose unit of the chitin material is 1.0. When the chitosan has an average degree of acetylation within the range of from 0 to about 0.5, the chitosan is generally water insoluble prior to protonation of the chitosan to provide the  
25 chitosan salts with the desired initial absorbency properties of the present invention. However, one skilled in the art will appreciate that other characteristics, such as the actual pattern of acetyl groups of the chitosan, may also have an effect on the water-solubility of the chitosan salt.

30 Chitosan and chitosan salts may generally have a wide range of molecular weights. Chitosan and chitosan salts having a relatively high molecular weight are often beneficial for use in the present invention. Nonetheless, a wide range of molecular  
35 weights is suitable for use in the present invention. It is generally most convenient to express the molecular weight of a chitosan or chitosan salt in terms of its viscosity in a 1.0 weight percent aqueous solution at 25°C. Since chitosan is

centipoise), and most suitably less than about 240 mPa·s (240 centipoise).

5 The process according to the present invention is found to produce an improvement in initial AUL values in chitosan salts over a wide range of molecular weights. While high molecular weight chitosan salts are generally preferred, it is important that improvements in low molecular weight chitosan salts can be achieved. This is because aqueous solutions of high molecular weight chitosan salts exhibit a high viscosity compared to an aqueous solution containing the same concentration of low molecular weight chitosan salts. Thus, for reasons of efficiency, it is often desirable to form an aqueous solution comprising the highest concentration of chitosan salt possible while still being able to effectively work with the aqueous solution.

20 The chitosan salts of the present invention have the ability to absorb a liquid while the chitosan salt is under an external pressure or load, herein referred to as Absorbency Under Load (AUL). Synthetic polymeric materials, such as polyacrylates, having a generally high ability to absorb while under a load, have been found to minimize the occurrence of gel-blocking when incorporated in absorbent products. The method by which the Absorbency Under Load is determined is set forth below in connection with the examples. The Absorbency Under Load values determined as set forth below and reported herein refer to the amount in grams of an aqueous solution, containing 0.9 weight percent sodium chloride, a gram of a material can absorb in 60 minutes under a load, for example, of about 2.07 kPa (0.3 pound per square inch (psi)). As a general rule, it is desired that the chitosan salt has an initial Absorbency Under Load value, for a load of about 2.07 kPa (0.3 psi), of at least about 14, beneficially of at least about 17, more beneficially of at least about 20, suitably of at least about 24, more suitably of at least about 27, and up to about 50 grams per gram. As used herein, the term "initial Absorbency Under Load" is meant to refer to that AUL value exhibited by a material as measured

their initial AUL value after aging for about 20 days at about 24°C and about 100 percent relative humidity.

5 As described above, the chitosan salt is suitably a chitosan carboxylate, such as chitosan acetate or chitosan formate, or a chitosan hydrohalide, such as chitosan hydrochloride. Such a chitosan carboxylate or chitosan hydrohalide has an initial Absorbency Under Load value of at least about 14, beneficially of at least about 17, more beneficially of at least about 20, 10 suitably of at least about 24, more suitably of at least about 27, and up to about 50, grams per gram. Beneficially, such a chitosan carboxylate or chitosan hydrohalide also retains greater than about 50 percent, suitably greater than about 70 percent, and more suitably greater than about 80 percent, of 15 its initial AUL value after aging for about 60 days at about 24°C and at least about 30 percent relative humidity and, beneficially, retains greater than about 50 percent, suitably greater than about 70 percent, and more suitably greater than about 80 percent of its initial AUL value after aging for about 20 20 days at about 24°C and about 100 percent relative humidity.

Without intending to be bound thereby, it is hypothesized that the aging phenomenon in regards to the AUL is due to the creation of crosslinking points or additional crosslinking 25 points of the chitosan salt. As a result of such crosslinking points or additional crosslinking points, the chitosan salt becomes more rigid or harder, resulting in the chitosan salt becoming less absorbent. Crosslinking points can generally be divided into two groups. First, crosslinking points can be of a 30 relatively permanent crosslinking, such as with ester or amide linkages, resulting, for example, from the use of a multicarboxylic crosslinking agent, or with coordination bonding, resulting, for example, from the use of a polyvalent metal ion crosslinking agent, or with physical crosslinks 35 resulting, for example, from a retained crystalline structure. Second, crosslinking points can be of a relatively temporary crosslinking, such as with hydrogen bonding within the chitosan salt. In order to improve the aging stability of the chitosan

In such a process, the chitosan is dispersed in a nonsolvent and an acid and water are added to the mixture. As used herein, the term "nonsolvent" is meant to represent a nonaqueous liquid that is miscible with water and in which both chitosan and the chitosan salt to be formed are insoluble. Examples of nonsolvents useful in the present invention include methanol, ethanol, acetone, isopropanol, dioxane, glycerol, ethylene glycol, propylene glycol, butanol, pentanol, hexanol, and mixtures thereof. Suitable nonsolvents include methanol, ethanol, isopropanol, and mixtures thereof. The water and the nonsolvent are used in amounts in the mixture effective to result in the chitosan and the chitosan salt to be formed not being soluble in the mixture.

The acids are added to the mixture at conditions effective to allow the acids to react with and modify the chitosan to a chitosan salt while retaining an effective amount of the original crystallinity of the chitosan. Such effective conditions can vary and will typically depend on, for example, temperature, pressure, mixing conditions, and types and relative amounts of materials, nonsolvents, water and acids used. The chitosan salt is then generally recovered from the mixture as, for example, using the methods described herein. Such a final recovered crystalline-crosslinked chitosan salt comprises an amount of the original crystalline structure of the chitosan to be effective to result in the crystalline-crosslinked chitosan salt exhibiting an effective initial Absorbency Under Load value.

Chitosan is generally known to be highly crystalline material. The degree of crystallinity generally depends on the source of the chitosan and its processing history. The highly-ordered crystalline structures and the less-ordered amorphous areas generally have different accessibilities toward incoming chemicals such as acids. The result of this difference in accessibility is that the amorphous areas are, in the case of reaction with an acid, generally protonated first and heaviest, whereas the highly crystalline areas are protonated last and

acid is measured at about 25°C. In general, the weaker an acid, the higher its pKa value will be. The pKa values for acids at various temperatures are well known and may be found in any of many available references, such as in the CRC Handbook of Chemistry & Physics, 75th Edition, edited by David R. Lide, pages 8-45, CRC Press (1994).

As used herein, the term "monobasic acid" is intended to represent an acid having one displacable hydrogen atom per molecule. The monobasic acids should have a pKa<sub>1</sub> less than about 6, suitably less than about 5.5, and more suitably less than about 5 as measured at the conditions under which the acid is being used in the process. Examples of monobasic acids having a pKa<sub>1</sub> less than about 6, when the pKa<sub>1</sub> is measured at about 25°C, include hydrochloric, hydrobromic, hydrofluoric, hypochlorous, iodic, nitrous, perchloric, periodic, acetic, acetoacetic, acrylic, adipamic, m-aminobenzoic, p-aminobenzoic, o-aminobenzenesulfonic, m-aminobenzenesulfonic, p-aminobenzenesulfonic, anisic, o-β-anisylpropionic, m-β-anisylpropionic, p-β-anisylpropionic, barbituric, benzoic, benzenesulfonic, bromoacetic, o-bromobenzoic, m-bromobenzoic, n-butyric, iso-butyric, n-caproic, iso-caproic, chloroacetic, o-chlorobenzoic, m-chlorobenzoic, p-chlorobenzoic, α-chlorobutyric, β-chlorobutyric, γ-chlorobutyric, o-chlorocinnamic, m-chlorocinnamic, p-chlorocinnamic, o-chlorophenoxyacetic, m-chlorophenoxyacetic, o-chlorophenylacetic, m-chlorophenylacetic, p-chlorophenylacetic, β-(o-chlorophenyl) propionic, β-(m-chlorophenyl) propionic, β-(p-chlorophenyl) propionic, α-chloropropionic, β-chloropropionic, cis-cinnamic, trans-cinnamic, crotonic (trans-), cyanoacetic, γ-cyanobutyric, o-cyanophenoxyacetic, m-cyanophenoxyacetic, p-cyanophenoxyacetic, cyanopropionic, dichloroacetic, dichloroacetylacetic, dihydroxybenzoic (2,2-), dihydroxybenzoic (2,5-), dihydroxybenzoic (3,4-), dihydroxybenzoic (3,5-), dihydroxymalic, dihydroxytartaric, dimethylmalonic, dinicotinic, dinitrophenol (2,4-), dinitrophenol (3,6-), diphenylacetic,

It is believed that the use of monobasic acids having a  $pK_{a1}$  greater than about 6 generally will not result in chitosan salts exhibiting the desired initial Absorbency Under Load properties because such acids are too weak to sufficiently protonate the chitosan to form the desired chitosan salt.

As used herein, the term "multibasic acid" is intended to represent an acid having more than one displacable hydrogen atom per molecule. Examples of multibasic acids having a  $pK_{a1}$  less than about 6 and all  $pK_{an}$  greater than about 5.5, wherein  $n$  is an integer greater than 1, include arsenic, chromic, o-phosphoric, phosphorous, sulfurous, tellurous, tetraboric, ascorbic, DL-aspartic, cyclohexane-1:1-dicarboxylic, cyclopropane-1:1-dicarboxylic, dimethylmalic, o-hydroxybenzoic, m-hydroxybenzoic, p-hydroxybenzoic, and maleic, and mixtures thereof.

In contrast, examples of multibasic acids that do not have a  $pK_{a1}$  less than about 6 and all  $pK_{an}$  greater than about 5.5, wherein  $n$  is an integer greater than 1, include o-boric, carbonic, germanic, hydrogen sulfide, pyrophosphoric, m-silicic, o-silicic, telluric, adipic, citric, DL-cysteine, L-cystine, fumaric (trans-), glutaric, oxalic, o-phthalic, m-phthalic, p-phthalic, itaconic, malic, malonic, mesaconic, methylsuccinic, succinic,  $\alpha$ -tartaric, and meso-tartaric. Such acids may have a  $pK_{a1}$  greater than about 6 or a  $pK_{an}$  less than about 5.5.

It is believed that the use of a multibasic acid having a  $pK_{a1}$  greater than about 6 generally will not result in chitosan salts exhibiting the desired initial Absorbency Under Load properties because such acids are too weak to sufficiently protonate the chitosan to form the desired chitosan salt. It is believed that the use of a multibasic acid having a  $pK_{an}$  less than about 5.5 results in chitosan salts that generally do not exhibit the desired initial Absorbency Under Load properties, because such a multibasic acid essentially acts as a crosslinking agent and generally results in too much crosslinking of the chitosan salt,

The presence of a crosslinking agent, in certain embodiments of processes of the present invention, may improve the initial Absorbency Under Load value of a chitosan salt when compared to an otherwise essentially identical chitosan salt without a crosslinking agent in an otherwise essentially similar process. As such, a crosslinking agent may optionally be used in the process of the present invention.

Crosslinking agents suitable for use in the present invention are generally water soluble. One suitable crosslinking agent is a compound having at least two functional groups or functionalities capable of reacting with the amido, amino, or hydroxyl groups of a chitosan salt. It is desired that such a crosslinking agent be selected from the group consisting of organic compounds such as dialdehydes, multicarboxylic acids, diepoxides, and mixtures thereof. Specifically, the crosslinking agent may be selected from the group consisting of glutaraldehyde, citric acid, butane tetracarboxylic acid, carboxymethyl cellulose, poly(ethylene glycol) diglycidal ether, and bis[polyoxyethylene bis(glycidyl ether)], and mixtures thereof.

Another suitable crosslinking agent is a multibasic acid having both a  $pK_{a1}$  and a  $pK_{a2}$  that are both less than about 5.5. Such an acid may have more than two displacable hydrogen atoms per molecule wherein the  $pK_{a_m}$  is less than or greater than 5.5, wherein  $m$  is an integer greater than 2. Examples of such acids useful as crosslinking agents herein include pyrophosphoric acid, adipic acid, butane tetracarboxylic acid, citric acid, glutaric acid, itaconic acid, malic acid, malonic acid, mesaconic acid, methylsuccinic acid, oxalic acid, o-phthalic acid, m-phthalic acid, p-phthalic acid, succinic acid, alpha-tartaric acid, and meso-tartaric acid. Suitably, the crosslinking agent is selected from adipic acid, butane tetracarboxylic acid, citric acid, glutaric acid, itaconic acid, malic acid, succinic acid, and mixtures thereof.

mixed together. This is so that the chitosan does not become crosslinked before it is able to be converted to the desired chitosan salt or that the chitosan salt becomes too crosslinked before it is sufficiently protonated. It is particularly  
5 beneficial to add the crosslinking agent after the other materials have been mixed together when the crosslinking agent, such as glutaraldehyde, substantially crosslinks the chitosan salt in the mixture as compared to substantially crosslinking the chitosan salt during a later, post-recovery treatment  
10 process.

The aqueous mixture of a chitosan, water, acid, and optionally a crosslinking agent should be prepared under conditions effective to form a chitosan salt. Thus, the mixture can generally be  
15 formed at any temperature at which the prepared chitosan salt will be soluble in the water. Generally, such temperatures will be within the range of from about 10°C to about 100°C. As a general rule, it is suitable to form the mixture with agitation.

It has been found that the aqueous mixture must be acidic in order to achieve a chitosan salt that exhibits the desired absorbent properties of the present invention. In particular, it is desired that the mixture used to prepare the chitosan salts of the present invention have an equilibrium pH between  
20 about 2 to about 6.5, suitably between about 2.5 to about 6, and more suitably between about 4 to about 6. Mixtures having an equilibrium pH that is either too low or too high have generally been found to not result in chitosan salts exhibiting the desired absorbent properties. As used herein, the term  
25 "equilibrium pH" is meant to represent the pH of the mixture used to prepare the chitosan salt of the present invention when the mixture has reached equilibrium or, in other words, a steady state. In such a mixture at equilibrium, the chitosan will generally have substantially reacted with the acid to form the  
30 desired chitosan salt.  
35

The chitosan salts of the present invention are suitable for use in disposable absorbent products such as personal care products,



general rule, the chitosan salt can be recovered by evaporative drying at a temperature within the range of from about 10°C to about 100°C, suitably from about 40°C to about 60°C. Naturally, higher temperatures can be employed if the mixture is placed under pressure. Lower temperatures can be employed if the mixture is placed under a vacuum.

Other methods of recovery include precipitation in which a precipitating agent, such as methanol, ethanol, isopropanol, or acetone is added to the mixture to precipitate the chitosan salt and the crosslinking agent, if used, out of the mixture. The chitosan and the crosslinking agent, if used, can then be recovered by filtration. If precipitation is used to recover the chitosan salt, it may be desirable to wash the recovered chitosan salt to remove the precipitating agent.

Depending on the form in which the chitosan salt is recovered, it may be necessary or desirable to alter the form of the chitosan salt. For example, if evaporative drying is employed, the chitosan salt may be recovered in the form of a film or sheet. It may be desirable to comminute the film or sheet material into particles or flakes of material.

The form of the recovered chitosan salt desired will depend to a large extent on the use for which it is intended. When the chitosan salt is intended for use in absorbent personal care products, it is generally desired that the chitosan salt be in the form of a discrete particle, fiber or flake. When in the form of a particle, it is generally desired that the particle have a maximum cross-sectional dimension within the range from about 50  $\mu\text{m}$  to about 2,000  $\mu\text{m}$ , suitably within the range from about 100  $\mu\text{m}$  to about 1,000  $\mu\text{m}$ , beneficially within the range from about 300  $\mu\text{m}$  to about 600  $\mu\text{m}$ .

It may be desirable to treat a chitosan salt, after it has been recovered from the mixture in which it was prepared, under conditions effective to result in the chitosan salt becoming water swellable and water insoluble and exhibiting the desired

structure will result that acts as crosslinkage bonds within the structure of the chitosan salt. Providing the mixture with a relatively less volatile acid tends to lengthen the time of the crosslinking process, at a given temperature, compared to the use of a relatively more volatile acid. Nonetheless, similar general absorptive properties can generally be achieved with the use of either a volatile or a nonvolatile acid.

As used herein, a "volatile acid" or "an acid that is volatile" is intended to represent an acid that may be disassociated from the chitosan salt in which the acid is incorporated at a temperature less than about 200°C. In general, a volatile acid will be an acid that has a boiling point less than about 200°C. However, if the acid forms bonds that are too strong within the chitosan salt, such an acid may not be capable of being readily disassociated from the chitosan salt even though the acid has a boiling point less than about 200°C. Thus, for example, hydrochloric acid has a boiling point less than about 200°C but forms such strong bonds within the chitosan salt that the hydrochloric acid is essentially incapable of being disassociated from the chitosan salt even at temperatures up to about 200°C. Examples of acids suitable for use as a volatile acid herein include formic acid, acetic acid, propionic acid, butyric acid, and mixtures thereof. As used herein, a "nonvolatile acid" is intended to represent an acid that will not be disassociated from the chitosan salt in which the acid is incorporated at a temperature less than about 200°C. In general, a nonvolatile acid will have a boiling point greater than about 200°C or, as discussed above, has a boiling point less than about 200°C but forms such strong bonds within the chitosan salt that the acid will not easily disassociate from the chitosan salt. Examples of acids suitable for use as a nonvolatile acid herein include hydrochloric acid or phosphoric acid. In some instances, it may be desired to use both a volatile and a nonvolatile acid in the mixture used to prepare the chitosan salt. For example, a volatile acid, such as formic acid or acetic acid, may be used in combination with a nonvolatile acid such as hydrochloric acid or phosphoric acid.

absence of a crosslinking agent, heat treatment or humidity treatment of the chitosan salt is believed to result in a crystallization of the chitosan salt structure.

- 5 There is generally an optimum degree or amount of crosslinking of a particular chitosan salt that optimizes the initial Absorbency Under Load value and, desirably, the aging stability of the particular chitosan salt. If too little crosslinking occurs, the chitosan salt may possess a relatively low initial  
10 Absorbency Under Load value due to a lack of gel strength. If too much crosslinking occurs, the chitosan salt may similarly have a relatively low initial Absorbency Under Load value due to the inability of the chitosan salt to absorb liquid.
- 15 Any method of recovering the chitosan salt from a mixture, without unacceptably deteriorating the absorption characteristics of the chitosan salt, is suitable for use in the present invention. Examples of such methods include evaporative drying, freeze drying, precipitation, critical point drying, and  
20 the like.

Those skilled in the art will recognize that the presence of crosslinks formed by either chemical bonds such, as esterification, or by physical structure crystallization can  
25 generally be detected through various analytical techniques. For example, infrared spectroscopy, X-ray diffraction, and nuclear magnetic resonance can be used to verify the presence of chemical bonding and physical structure crystallite crosslinks.

- 30 In another aspect, the present invention relates to a water-swellaable, water-insoluble chitosan salt characterized in that the chitosan salt possesses crosslinks formed by chemical bonding or physical structure crosslinking. Such a chitosan salt is suitably formed by the methods described above.
- 35 Nonetheless, the described methods are not intended to be the exclusive methods by which such a chitosan salt can be formed.

Corporation, the thickness meter contains a spring attached to the probe within the meter housing. This spring is removed to provide a free-falling probe which has a downward force of about 27 grams. In addition, the cap over the top of the probe, located on the top of the meter housing, is also removed to enable attachment of the probe to the suspension spring 5 (available from McMaster-Carr Supply Co., Chicago, Illinois, Item No. 9640K41), which serves to counter or reduce the downward force of the probe to about  $1 \text{ gram} \pm 0.5 \text{ gram}$ . A wire hook can be glued to the top of the probe for attachment to the suspension spring. The bottom tip of the probe is also provided with an extension needle (Mitutoyo Corporation, Part No. 131279) to enable the probe to be inserted into the sample cup.

15 To carry out the test, a 0.160 gram sample of the absorbent material, which has been sieved to a particle size between 300 and 600  $\mu\text{m}$ , is placed into the sample cup. The sample is then covered with a plastic spacer disc, weighing 4.4 grams, which is slightly smaller than the inside diameter of the sample cup and serves to protect the sample from being disturbed during the test. The 100 gram weight is then placed on top of the spacer disc, thereby applying a load of about 2.07 kPa (0.3 pound per square inch). The sample cup is placed in the Petri dish on the platform and the laboratory jack raised up until it contacts the tip of the probe. The meter is zeroed. A sufficient amount of saline solution is added to the Petri dish (50-100 milliliters) to begin the test. The AUL can be determined by determining the weight difference between the sample cup before and after the test, the weight difference being the amount of solution absorbed by the sample. The weight of saline solution absorbed after about 60 minutes is the AUL value expressed as grams saline solution absorbed per gram of absorbent. If desired, the readings of the modified thickness meter can be continuously inputted to a computer (Mitutoyo Digimatic Miniprocessor DP-2 DX) to make the calculations and provide AUL readings. As a cross-check, the AUL can also be determined by determining the distance the 100 gram weight is raised by the expanding sample as it absorbs the saline solution, as measured by the probe.

stirred for several hours during which the chitosan reacted with the acids to form chitosan salts which dissolved into the solution. The equilibrium pH of the mixture was measured after dissolution of the chitosan salt into the solution. The  
5 obtained liquid mixtures were then treated with various amounts of a 2.5 weight per cent aqueous solution of glutaraldehyde homogenized by thoroughly stirring by hand and then air dried at about 23°C for about 16 hours on a Petri dish. After such drying, the solid materials were ground in a Waring blender and  
10 a fraction of particulates (300  $\mu\text{m}$  to 600  $\mu\text{m}$ ) was collected for each sample for measurement of the AUL. The AUL measurements, type of acid used, the equilibrium pH of the mixture, and the amount of glutaraldehyde solution used, given as a weight percent based on the weight of chitosan used, for these samples  
15 are shown in Table 2.

After such drying, the solid materials were ground in a Waring blender and a fraction of particulates (300  $\mu\text{m}$  to 600  $\mu\text{m}$ ) was collected for each sample for measurement of the AUL. The AUL measurements and the amount of glutaraldehyde solution used for these samples are shown in Table 3.

TABLE 3

Starting Chitosan Material	Amount of glutaraldehyde (weight %)	Initial AUL (g/g)
Chitosan A	0.7	11.7
Chitosan A	1.1	9.9
Chitosan A	2.2	8.1
Chitosan B	0.35	17.6
Chitosan B	0.9	17.6
Chitosan B	1.6	15.1
Chitosan C	0.35	24.1
Chitosan C	0.7	20.3
Chitosan C	1.1	17.5

Example 3

Chitosan C (4.5 grams) was mixed with about 188 grams of aqueous solution of hydrochloric acid. The mixtures were stirred for several hours during which the chitosan reacted with the acid to form chitosan hydrochloride which dissolved into the solution. The solutions all had an equilibrium pH between about 5.0 and 5.5. The obtained liquid mixture was then treated with various amounts of aqueous solutions of various crosslinking agents. The mixture was then homogenized by thoroughly stirring by hand and then air dried at about 23°C for about 16 hours on a Petri dish. After such drying, the solid materials were ground in a Waring blender and a fraction of particulates (300  $\mu\text{m}$  to 600  $\mu\text{m}$ ) was collected for each sample for measurement of the AUL. The AUL measurements and the crosslinker type and amount for these samples, given as a weight percent based on the weight of chitosan used, are shown in Table 4. In Table 4, the number in

Example 5

Samples of various chitosans (20 grams) were individually added into 1000 ml of distilled water to form a 2% suspension. Acetic acid (8.5 grams) or formic acid (5.7 grams) was added into the suspension while stirring. The resulting mixtures containing water, chitosan, and acid were then thoroughly mixed for at least 5 hours at 23°C. The equilibrium pH of the mixture was then measured. The completely dissolved chitosan salt was recovered from the solution by evaporative drying at 50°C in a Blue M air-convection oven. After drying, the recovered chitosan salt was ground into granules in a blender and heat treated at various temperatures for specific times. The initial Absorbency Under Load values of the various chitosan salts so prepared were measured. The exact combination of chitosan and acid and its peak AUL value are set forth in Table 5.

Example 6

Samples of Chitosan C and Chitosan F (20 grams) were individually added into 1000 ml of distilled water to form a 2% suspension. Formic acid (5.7 grams), 7.2 grams of acetic acid, 8.7 grams of propionic acid, 11.7 grams of 37 wt% of hydrochloric acid, 11.6 grams of phosphoric acid, 15.6 grams of glutaric acid, or 22.7 grams of citric acid were separately added into respective suspensions with agitation. Molar ratio of the acid to chitosan is 1 to 1. The resulting mixtures containing water, chitosan, and acid were then thoroughly mixed for at least 8 hours at about 23°C. The equilibrium pH of the mixture was then measured. The completely dissolved chitosan salt was recovered from the solution by evaporative drying at 40° C in a Blue M air-convection oven. After drying, the recovered chitosan salt was ground into granules in a blender and heat treated at various temperatures for specific times. The initial Absorbency Under Load values of the various chitosan salts so prepared were measured. The exact combination of chitosan and acid and its initial AUL value are set forth in Table 6.



Example 7

Samples of Chitosan F (20 grams) were added into 1000 ml of distilled water to form a 2% suspension. Formic acid (5.7 grams), 7.1 grams of acetic acid, 8.7 grams of propionic acid, or 11.7 grams of 37 wt% hydrochloric acid was added into the suspension with agitation. The molar ratio of the acid to chitosan was about 1 to 1. The resulting mixtures containing water, chitosan, and acid were then thoroughly mixed for at least 8 hours at 23°C. The equilibrium pH of each mixture was then measured. The mixture containing hydrochloric acid had an equilibrium pH of about 4.3. The mixtures containing the other acids each had an equilibrium pH of about 5.5. The completely dissolved chitosan salt was recovered from the solution by evaporative drying at 40°C in a Blue M air-convection oven. After drying, the recovered chitosan salt is ground into granules in a blender and placed in a chamber, which has a relative humidity of 100% at room temperature (about 23°C), and aged for 5, 10, 20, 30 and 40 days. The aged chitosan salts were then dried at ambient condition (30% to 50% relative humidity, room temperature (about 23°C)) for two days before measuring the aged AUL. The initial and aged Absorbency Under Load values of the various chitosan salts so prepared are measured. The exact combination of chitosan and acid and its AUL value are set forth in Table 7.

exact combination of chitosan and acid and its initial or aged AUL value are set forth in Table 8.

TABLE 8

5	Time of Aging (Days)	AUL (g/g)					
		Chitosan Formate	Chitosan HCOOH/HCL (3:1)	Chitosan HCOOH/HCL (1:1)	Chitosan Acetate	Chitosan HAC/HCL (3:1)	Chitosan HAC/HCL (1:1)
10	0	22.2	20.5	19.8	20.9	19.2	17.1
	10	18.8	18.1	18.6	14.3	16.7	14.9
	20	14.3	17.2	17.8	6.8	14.6	14.1
	30	10.1	14.1	16.2	--	--	--

#### Example 9

A sample of Chitosan D (20 grams) was suspended in 900 ml of distilled water with stirring. Thirty milliliters of mixed acid solution having a concentration of 1M acetic acid and 1M hydrochloric acid was added to the stirred chitosan suspension at room temperature (about 23°C). After 10 hours of mixing, the chitosan salt solution was titrated with the above-mentioned mixed acid solution until a transparent solution of chitosan salt having an equilibrium pH range of between about 5.2 and about 5.5 was obtained. The concentration of the chitosan salt solution was about 2 weight percent. Then, 0.026 gm of citric acid as a crosslinking agent (dissolved in 10 ml of distilled water) was added to the chitosan salt solution. In some cases, 0.013 gm of sodium hypophosphite was also added as a crosslinking catalyst. The solution is mixed well at 23°C, poured into Teflon-lined trays, and dried in a convection oven at 40°C for about 24 hours. Physical measurements of the chitosan salt generally indicate that substantially no crosslinking has occurred at this point. After grinding and sieving, the 300-600  $\mu$ m size fraction is cured at various temperatures for various lengths of time. The AUL results are set forth in Table 9.

The chitosan salt sample that was prepared without the sodium hypophosphite catalyst was cured at 100°C for 60 minutes and was

CLAIMS

1. A process for preparing a water-swellaable, water-insoluble chitosan salt, the process comprising:  
5 forming a mixture comprising a chitosan, water, and an acid selected from the group consisting of monobasic acids having a  $pK_{a1}$  less than about 6 and multibasic acids having a  $pK_{a1}$  less than about 6 and all  $pK_{a_n}$  greater than about 5.5, wherein  $n$  is an integer greater than 1, wherein the mixture  
10 has an equilibrium pH between about 2 and about 6.5, and wherein the mixture is prepared under conditions effective to form a chitosan salt; and recovering the chitosan salt from the mixture, wherein the chitosan salt is water swellaable and water insoluble.  
15
2. The process according to claim 1 wherein the chitosan is water-insoluble.
3. The process according to claim 1 or 2 wherein the water-swellaable and water-insoluble chitosan salt exhibits an  
20 initial Absorbency Under Load value of at least about 14 grams per gram.
4. The process according to claim 2 or 3 wherein the chitosan  
25 salt recovered from the mixture is water soluble.
5. The process according to claim 2, further comprising treating said recovered water-soluble chitosan salt at a temperature and for an amount of time effective to render  
30 said chitosan salt water swellaable and water insoluble.
6. The process according to claim 5, further comprising  
35 treating said recovered chitosan salt at a temperature above about 50°C for a time effective to render said chitosan salt water swellaable and water insoluble.

13. The process according to any of the preceding claims wherein the chitosan salt is chitosan hydrochloride, chitosan hydrobromide, chitosan phosphate, chitosan formate, chitosan acetate, chitosan propionate, chitosan chloroacetate, chitosan hydroxyacetate, chitosan butyrate, chitosan isobutyrate, chitosan acrylate, or mixtures thereof.
14. The process according to any of the preceding claims wherein the chitosan salt is chitosan hydrochloride, chitosan formate, chitosan acetate, chitosan propionate, or mixtures thereof.
15. The process according to any of the preceding claims wherein the acid is acetic acid, acrylic acid, n-butyric acid, isobutyric acid, chloroacetic acid, formic acid, hydrobromic acid, hydrochloric acid, hydroxy acetic acid, propionic acid, phosphoric acid, and mixtures thereof.
16. The process according to claim 15 wherein the acid is hydrochloric acid, formic acid, acetic acid, propionic acid, or mixtures thereof.
17. The process according to any of the preceding claims wherein the mixture further comprises a crosslinking agent and the crosslinking agent is recovered with the chitosan salt.
18. The process according to claim 17 wherein the crosslinking agent is selected from the group consisting of a compound comprising at least two functional groups capable of reacting with an amido, amino, or hydroxyl group of a chitosan salt or a metal ion with at least two positive charges and which is effective to form coordination bonds with the chitosan salt.
19. The process according to claim 17 or 18 wherein said crosslinking agent is selected from the group consisting of dialdehydes, multicarboxylic acids, diepoxides, and mixtures thereof.

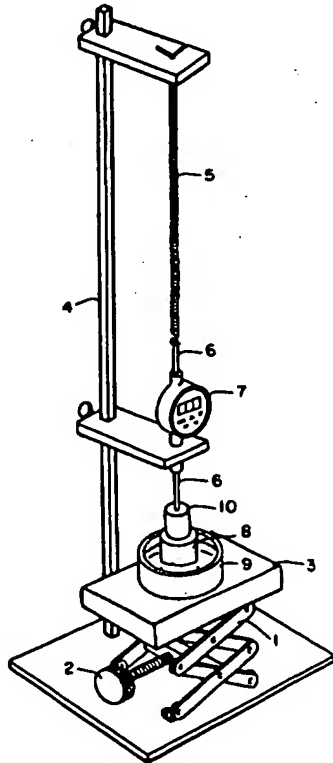
29. The process according to claim 28 wherein said mixture has an equilibrium pH between about 4 to about 6.
- 5 30. The process according to any of the preceding claims wherein the water-swellaable, water-insoluble chitosan salt exhibits an initial Absorbency Under Load value of at least about 17 grams per gram.
- 10 31. The process according to any of the preceding claims wherein the water-swellaable, water-insoluble chitosan salt exhibits an initial Absorbency Under Load value of at least about 20 grams per gram.
- 15 32. The process according to any of the preceding claims wherein the water-swellaable, water-insoluble chitosan salt retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24°C and at least about 30 percent relative humidity.
- 20 33. The process according to any of the preceding claims wherein the water-swellaable, water-insoluble chitosan salt retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 20 days at about 24°C and at about 100 percent relative humidity.
- 25 34. A water-swellaable, water-insoluble chitosan salt wherein the chitosan salt exhibits an initial Absorbency Under Load value of at least about 14 grams per gram.
- 30 35. The chitosan salt of claim 34 wherein the chitosan salt is chitosan hydrochloride, chitosan hydrobromide, chitosan phosphate, chitosan formate, chitosan acetate, chitosan propionate, chitosan chloroacetate, chitosan hydroxyacetate, 35 chitosan butyrate, chitosan isobutyrate, chitosan acrylate, or mixtures thereof.

days at about 24°C and at about 100 percent relative humidity.

- 5 45. The chitosan salt of claim 44 wherein the chitosan salt retains at least about 70 percent of the initial Absorbency Under Load value after aging for about 20 days at about 24°C and at about 100 percent relative humidity.
- 10 46. The chitosan salt of any of claims 34 to 45 wherein the chitosan salt has a viscosity in a 1.0 weight percent aqueous solution at 25°C of from about 100 mPa·s (100 centipoise) to about 80,000 mPa·s (80,000 centipoise).
- 15 47. A water-swellaable, water-insoluble chitosan salt obtainable by the process according to any of claims 1 to 33.

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(54) Title: CHITOSAN SALTS AND PROCESS FOR THE PREPARATION THEREOF			
(57) Abstract			
<p>Disclosed is a method for producing a water-swellaable, water-insoluble chitosan salt having improved absorption properties. The method involves forming a mixture of a chitosan, water, an acid, and, optionally, a crosslinking agent, recovering the formed chitosan salt from the mixture and, optionally, treating said recovered chitosan salt with heat or under humid conditions.</p>			
			

# INTERNATIONAL SEARCH REPORT

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## B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 627 225 (HÜLS AKTIENGESELLSCHAFT) 7 December 1994  see claims; examples ---	1-4, 13-20, 34-47
X	DATABASE WPI Week 8935 Derwent Publications Ltd., London, GB; AN 89-251834 XP002002628 & JP,A,01 182 302 (UNITIKA KK) , 20 July 1989 see abstract --- -/-	1

☒ Further documents are listed in the continuation of box C.

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